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An overview—Functional nanomaterials for lithium rechargeable batteries, supercapacitors, hydrogen storage, and fuel cells

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ABSTRACT

There is tremendous worldwide interest in functional nanostructured materials, which are the advanced nanotechnology materials with internal or external dimensions on the order of nanometers. Their extremely small dimensions make these materials unique and promising for clean energy applications such as lithium ion batteries, supercapacitors, hydrogen storage, fuel cells, and other applications. This paper will highlight the development of new approaches to study the relationships between the structure and the physical, chemical, and electrochemical properties of functional nanostructured materials. The Energy Materials Research Programme at the Institute for Superconducting and Electronic Materials, the University of Wollongong, has been focused on the synthesis, characterization, and applications of functional nanomaterials, including nanoparticles, nanotubes, nanowires, nanoporous materials, and nanocomposites. The emphases are placed on advanced nanotechnology, design, and control of the composition, morphology, nanostructure, and functionality of the nanomaterials, and on the subsequent applications of these materials to areas including lithium ion batteries, supercapacitors, hydrogen storage, and fuel cells.

1. Introduction

For a clean environment, batteries (alone or in combination with supercapacitors) for electric vehicles (EVs), hybrid electric vehicles (HEVs), or large-scale hydrogen fuel cells are believed to be the key to reducing our dependence on oil. Currently, among all the different kinds of rechargeable batteries, the Li-ion batteries (LIBs) will be the best choice for powering EVs and HEVs. There are serious challenges for further development of Li rechargeable batteries for electric vehicles [1], however. The lithium ion batteries [2–6] still cannot meet the required combinations of high energy density, high power, and high rate capability. Supercapacitors can be charged and discharged very quickly and are possible as an alternative power source; however, they are expensive, as they are made of expensive oxides (such as RuO_2 and IrO_2, which show high specific capacitance) that are only available in scarce quantities [7].

Hydrogen, another energy storage alternative, may be stored as a gas, a liquid, or bonded within a solid material. The latter is the safest approach, and hydrogen storage in this form has a relatively high volumetric capacity [8,9]. Up to now, however, no hydride system has been found to meet all of the demands of mobile (fuel storage, internal combustion, fuel cell) applications. Such gas-phase applications await novel technologies to further improve the hydrogen storage capacity and reversibility. In direct methanol fuel cells (DMFCs) or direct alcohol fuel cells (DAFCs), and the proton exchange membrane fuel cells (PEMFCs), the anodic oxidation of combustibles and the cathodic reduction of oxygen should be catalyzed to occur at adequate rates at low temperatures [10]. To develop catalysts with high activity, reasonable reliability, and durability, in combination with cost reduction, is an important task.

2. Applications of functional nanostructured materials

Functional nanomaterials are advanced nanotechnology materials with internal or external dimensions on the order of nanometers. These extremely small dimensions make these materials unique and promising for clean energy areas such as lithium ion batteries [11–25], supercapacitors [19,26–28], hydrogen storage [29,30], fuel cells [31–33], and other applications. Some examples from our recent work demonstrate that nanostructured materials can play significant role in improving the electrochemical performance of proposed alternative electrode materials.

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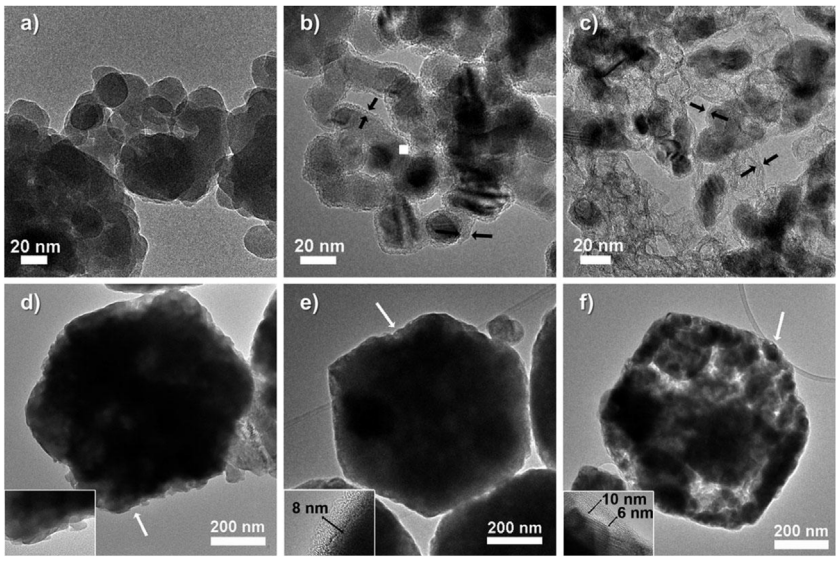

Fig. 1. TEM images showing the formation of germanium/carbon nanostructures from the germanium oxide precursors: (a) GeO_2 nanoparticles, (b) carbon-coated GeO_2 nanoparticles, (c) C-Ge/C. The black arrows in (b,c) indicate that the carbon shells have a thickness of about 3 nm.
Adopted from Ref. [21].

2.1. Functional nanostructured materials for lithium ion batteries

Graphite and $LiCoO_2$ are the commercial anode and cathode materials, respectively, since the introduction of LIBs in the 1990s. There two issues for the electrode materials: (1) lithium storage capacities are still not enough for the market requirements and (2) to improve both the cycling stability and the rate capability is a great challenge. Thus much research has been focused on high capacity materials such as silicon (4200 mAh g^{-1}), germanium (1623 mAh g^{-1}), tin (993 mAh g^{-1}) and transition metal oxides (100–500 mAh g^{-1}) to replace the graphite (372 mAh g^{-1}) anode, however, there is a large volume expansion and contraction problem associated with Li^+ insertion and removal reactions, respectively; and new cathode material $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (for portable electronics due to safety and low cost), spinel $LiMn_2O_4$ and olivine $LiFePO_4$ (for transportation applications due to chemical stability and high charge–discharge rate capability) are promising for replacing commercial cathode material $LiCoO_2$.

As Si/graphene composite can accommodate large volume changes of Si and maintain good electronic contact, nano-Si/graphene composite shows enhanced electrochemical performance, with a lithium storage capacity of 1168 mAh g^{-1} and coulombic efficiency of 93% up to 30 cycles [20].

It is interesting that a cluster-type nanostructure and a non-clustered structure (Fig. 1) have different effects on the electrochemical performance of different composites of clustered-Ge/carbon (C-Ge/C) and non-clustered-Ge/carbon (NC-Ge/C). The NC-Ge/C structure showed very poor capacity retention at rates over 1 C, while the C-Ge/C structure showed an exceptionally high rate capability up to the 40 C rate (64 A g^{-1}) [21], which means that this composite as anode material of a lithium ion battery could be charged to full capacity in 1.25 min. Although the high price of germanium is a drawback for the commercialization of this anode material, the C-Ge/C composite has the potential for being a high-energy and high-power anode material for lithium-ion batteries.

Hollow-structured α-Fe_2O_3/carbon nanocomposite with a high surface area of around 260 m^2 g^{-1} (Fig. 2), synthesized by a one-step, in situ, and industrially oriented spray pyrolysis method, showed a high capacity of 1210 mAh g^{-1} at a current density of 0.1 C (100 mA g^{-1}), enhanced rate capability, and excellent cycling stability (720 mAh g^{-1} at a current density of 2 C up to 220 cycles) [22]. The reasons are (1) the high-surface-area hollow structure composed of thin nanosheets can facilitate the contact between active materials and the electrolyte, and shorten the lithium diffusion length; (2) the well dispersed small α-Fe_2O_3 nanocrystals in the amorphous carbon which can accommodate the volume changes caused by lithium insertion and de-insertion, and could also enhance the electron transport to/within the α-Fe_2O_3 particles or crystals.

A strategy to employ graphene as supporting sheets for loading nanosized SnO_2 particles with carbon coating layers [23] has significantly improved the cycling performance, compared to SnO_2/graphene and SnO_2/carbon, as anode material for lithium ion batteries. This is because the graphene sheets and the carbon coating layer enhance the conductivity and buffer the volume changes of nanosized SnO_2 particles. A high capacity of 757 mAh g^{-1} was retained after 150 cycles at current density of 200 mA g^{-1}.

A novel nanocrystalline porous α-$LiFeO_2$–C composite with a high surface area of around 115 m^2 g^{-1} (Fig. 3) [24] delivered a significantly higher reversible capacity and excellent cycling stability (230 mAh g^{-1} at 0.5 C after 100 cycles). Even at the high rate of 3 C, the electrode showed more than 50% of the capacity at low rate (0.1 C). The excellent electrochemical performance of this nanocomposite electrode is due to the porous conductive architecture among the nanoparticles, which decreases the absolute volume changes and increases the mobility of lithium ions, also offering conductive pathways along the whole interconnected wall in the structure, which is favourable for the transport of electrons, promotes liquid electrolyte diffusion into the bulk materials, and acts as a buffer zone to absorb the volume changes.

$LiFePO_4$–Fe_2P–C composite prepared by a simple ultra-fast solvent assisted manual grinding method, combined with solid state reaction, showed specific capacity of 167 mAh g^{-1} at 0.2 C and 146 mAh g^{-1} at 5 C for 100 cycles, respectively. At the high current density of 1700 mA g^{-1} (10 C rate), it exhibited long-term cycling stability, retaining around 96% (131 mAh g^{-1}) of its original discharge capacity beyond 1000 cycles (Fig. 4), which can meet the requirements of a lithium-ion battery for large-scale power applications [25]. The superior high rate performance, and long-term cycling stability of the $LiFePO_4$–Fe_2P–C (5.8 wt.% C) electrode